Guided Terahertz Waves for Characterizing Explosives

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The Problem: One of the most promising and discussed applications of terahertz (THz) spectroscopy is the detection of explosives materials through identification of their vibrational fingerprint spectra. While much progress has been made toward the measurement of THz vibrational fingerprints of explosives,[1] fundamental issues remain to be addressed for THz sensing of explosives to reach its full potential. One issue is that line broadening mechanisms obscure the vibrational spectra of explosives, such that individual vibrational absorption lines merge into broad absorption features. Such line broadening makes identification of explosives more difficult and also impedes a full understanding of the origin of the vibrational fingerprint lines. A detailed scientific understanding of THz vibrational fingerprint spectra is necessary for their rational use in a database of threat materials. A second issue is that THz vibrational transitions tend to be about 100 times weaker relative to mid-infrared vibrational transitions. This emphasizes a need to develop methods to boost the sensitivity of THz measurements for explosives detection.

The Solution: Researchers at NRL and Oklahoma State University (OSU) have collaborated to make innovative use of the metal parallel plate waveguide (PPWG) to measure vibrational fingerprint spectra of explosives solids with unprecedented narrow lineshapes. This approach builds upon previous work by OSU that demonstrated the suitability of the PPWG for performing sensitive THz spectroscopic measurements.[2,3] In a PPWG, THz waves are strongly confined in the narrow gap (20–100 microns) between the plates while propagating over a relatively long path of several centimeters (Fig. 1). We exploit this high sensitivity by depositing a thin film of an explosive (or simulant) on one of the inner metal surfaces. We have used a variety of simple methods to produce thin films of suitable polycrystalline quality, including casting from solution and vacuum sublimation. The measurement method outlined in Fig. 1 is called waveguide terahertz time-domain spectroscopy (THz-TDS),[3,4] and uses well established ultrafast opto-electronic

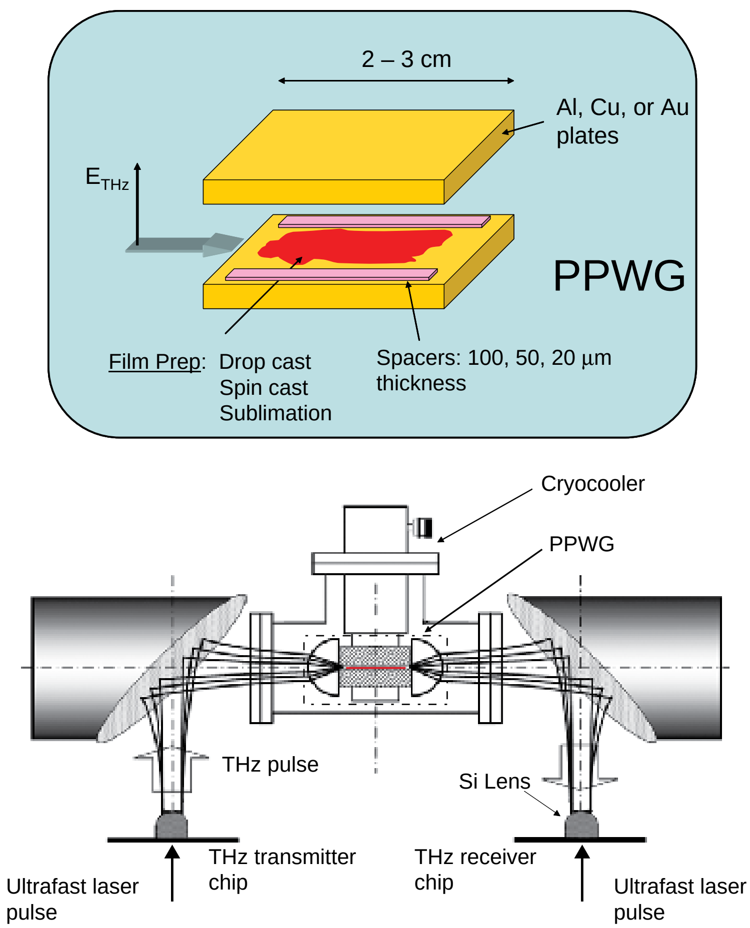

FIGURE 1
Top: Schematic of the metal parallel plate waveguide containing a thin film. Bottom: Schematic of waveguide terahertz time-domain spectroscopy.

techniques to generate and detect sub-picosecond THz pulses.

Vibrational Fingerprints as Narrow as Gas Lines: Virtually all previous THz measurements of explosives solids have suffered from line broadening due to sample disorder. Consequently, the fundamental underlying THz vibrational fingerprint spectrum of explosives and related materials has remained unknown. We have demonstrated the first-ever resolution of these underlying fingerprints using waveguide THz-TDS at cryogenic temperatures.[5,6] In Fig. 2 we compare the THz responses of the explosive simulant 2,4-dinitrotoluene (2,4-DNT) as a film in an aluminum PPWG, and in conventional pellet form, where 2,4-DNT is randomly dispersed in a transparent polyethylene matrix. The persistent ringing patterns of the signal waveforms are the result of THz absorption by vibrational modes. Note that the oscillatory pattern for the pellet sample decays to the noise floor in about 20 picoseconds, whereas the oscillations for the film persist beyond 100 picoseconds. The corresponding vibrational absorption spectra are derived by Fourier transformation of the time-dependent signals (Fig. 2 bottom). The vibrational spectrum of the film shows a dramatic line narrowing effect and resolves several broad absorption features observed in the pellet spectrum. For the film, at least 19 lines are resolved between 0.5 and 2.5 THz, compared to fewer than 10 lines in the pellet sample. Some of the fingerprint lines in the film are as sharp as 7 GHz (0.21 cm^{-1}), which is as narrow as a molecular rotational-vibrational gas line at ambient pressure.

Figure 3 shows that waveguide THz-TDS resolves the previously unseen underlying vibrational fingerprint spectra of the explosives cyclotrimethylenetrinitramine (RDX) and trinitrotoluene (TNT). A highly detailed fingerprint spectrum results for both explosives, showing 18 lines for RDX and 21 lines for TNT. Several of the vibrational lines have linewidths narrower than 10 GHz. A sensitivity enhancement provided by the PPWG is highlighted by the relatively small mass of the explosives films, consisting of approximately 150 micrograms. This represents about 1% of the analyte mass typically needed in THz measurements of standard pellet samples of explosives to achieve similar signal levels.

Structural characterization of the explosives films using optical microscopy and X-ray diffraction indicates a planar ordering of the film on the PPWG surface, where individual micro-crystals form with high crystalline quality (e.g., see Fig. 3). We suggest that the sharp vibrational fingerprint lines observed in our films result from a high degree of crystalline order, which minimizes inhomogeneous line broadening.

Summary and Impact: We have demonstrated a new waveguide-based method for THz characterization

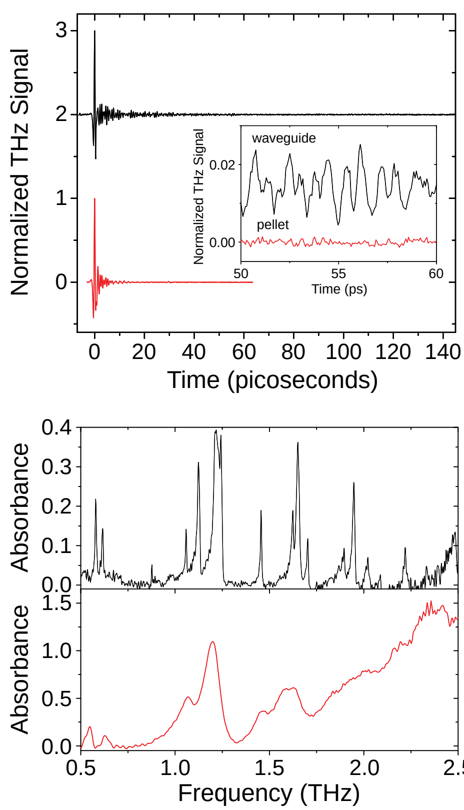

FIGURE 2
Top: Comparison of signal waveforms for pellet (red line) and waveguide THz-TDS (black line) characterizations of 2,4-DNT at 11 K. Bottom: Corresponding absorbance spectra for 2,4-DNT in pellet form (red line) and as a film (black line). An aluminum PPWG is used for waveguide THz-TDS.

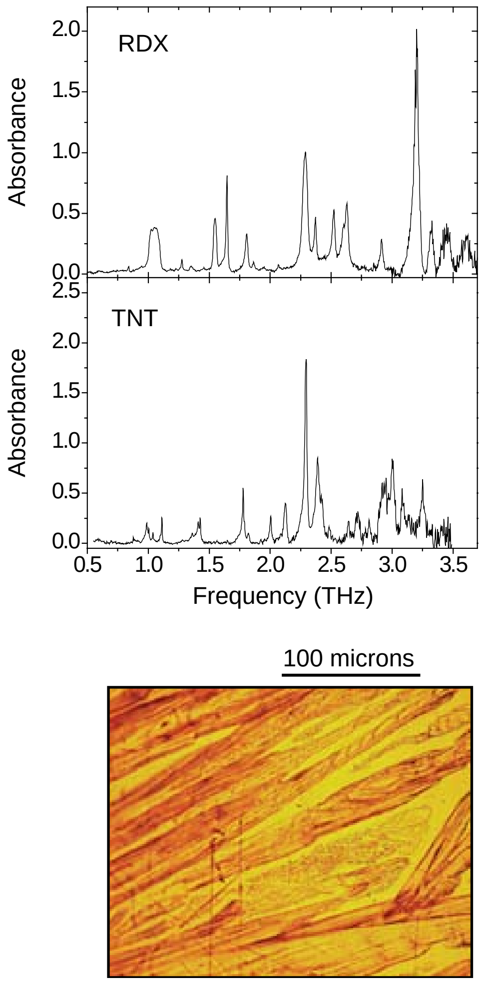

FIGURE 3
Top spectrum: Absorbance spectrum of an RDX thin film in an aluminum PPWG at 13 K. Bottom spectrum: Absorbance spectrum of a TNT thin film in a gold-coated PPWG at 12 K. The optical micrograph shows the TNT film on gold-coated PPWG.

of solids which has resulted in unprecedented narrow-line, high-sensitivity measurements of explosives and related materials. From a fundamental perspective, waveguide THz-TDS provides rigorous input to advance theoretical methods for calculating THz vibrational spectra, which can lead to deeper scientific understandings of the vibrational properties of solid-state materials. More practically, waveguide THz-TDS represents a gateway for the future development of THz-based point detection and forensic analysis of explosives and other threat materials. Further, high-resolution waveguide THz-TDS spectra can augment THz fingerprint databases used for remote sensing applications.

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